

Internal diffusion

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Abstract

Some minerals, such as rutile, hematite and ilmenite, found as inclusions in sapphires are capable of imparting body-colour to their host during high temperature heat treatment. The inclusions are cannibalized by the host sapphire for the chromophoric elements they contain. If the inclusions are not completely consumed by their host this 'internal diffusion' results in a zone of intensely coloured sapphire surrounding the remaining inclusions.

Introduction

The elemental causes at the atomic level of both the blue and the stable yellow colour in sapphires have been known and at least partially understood for some time. Over the past several years some excellent articles have been written by a number of well known and highly regarded gemmologists and research scientists that document these coloration mechanisms and the trace elements responsible for the resulting colour (Crowningshield and Nassau, 1981; Gunaratne, 1981; Nassau, 1981 and 1984; Keller, 1982; Schmetzer, Bosshart, and Hänni, 1983).

However, although the colour producing mechanism is generally understood and the colouring agent(s) is/are known, the exact source of the colouring agent(s) themselves is usually not mentioned and still remains, at least in some cases, unknown.

It seems to be generally accepted that the agents responsible for the blue and stable yellow colours in heat treated sapphires are either already naturally present as trace elements at the submicroscopic lattice level, as in the case of Sri Lankan 'geuda', or must be added in artificially from the exterior of the gem through a high temperature diffusion treatment.

In the case of a high temperature diffusion treatment the sources of the various colouring elements are jars of readily available purified laboratory chemicals, usually in oxide form, that are painted on to the prefaceted gem's surfaces just before treatment. The question of colouring element source only arises when we consider those gems that require no externally applied chemicals to attain body colour when they are subjected to a high

temperature treatment. Are all these colouring agents, in, as an example the Sri Lankan geuda, already present throughout the gems as trace elements, or is there some other natural source that provides at least some of the colouring ions from within the gems?

In his paper on geuda sapphire coloration written in 1981 Herbert S. Gunaratne of the Sri Lankan State Gem Corporation hinted at a possible chromophore source with the following statement:

'Titanium and iron are both colouring elements to which is attributed responsibility for imparting colour to blue sapphires. These elements have been found in varying proportions as insignificant impurities which are jointly or by themselves responsible for the colour. In the geuda of the ideal stone the rutile present has remained, so to say, in a state of inactivity, in the sense that its true function as a colouring element has not fully revealed itself. On the other hand, the faint powder-blue tint in such a stone could be attributed to iron in some form, which, if subject to heat, totally disappears at certain temperatures, making the stone visibly whitish. On being subject to still higher temperatures (temperature closer to the melting point of titanium), the titanium begins to melt within the host while the host is still in a solid state. In this state the atoms of the rapidly melting titanium not only begin to readjust themselves once again in relation to crystallographic laws, but also to bring out its colouring properties which gradually diffuse into the host.'

Although Mr. Gunaratne does not specifically say so, from the paragraph quoted above it can be reasonably inferred that when he writes of titanium melting he is referring to the mineral rutile in the form of exsolution needles and not to metallic titanium in uncombined elemental form. In the last sentence he speaks of the colouring properties of the melting titanium (rutile) gradually diffusing into the stone. Although no mention as to where the iron (also needed for blue colour) is coming from, this still strongly suggests that he felt that the solid microscopically visible inclusions present in Sri

Lankan geuda sapphires were responsible, at least in some way, for the resulting blue colour by diffusion into the surrounding corundum host.

With respect to yellow coloured sapphires from sources such as Australia and Thailand it has also been theorized more than once that inclusions may at least play a partial role in the colorizing process during heat treatment.

An excellent paper on gem corundum from Thailand written by Dr Peter C. Keller, Associate Director of the Los Angeles County Museum of Natural History, and published in 1982, points out one possible colouring element source in colour-stable heat-treated yellow and orange sapphires. This particular discussion on colour-cause is quoted as follows:

'The actual mechanism for the appearance of the golden yellow colour in the sapphire is open to speculation until the extensive research required to provide a conclusive answer can be completed. According to George Rossman, of the California Institute of Technology (personal communication, 1982). Trivalent iron alone will produce a pale yellow colour, but cannot be called upon for the rich golden colour observed in many of the treated stones seen in Chanthaburi. Rossman suggests that perhaps we are seeing incipient exsolution of the trivalent iron as sub-microscopic iron oxides in the corundum lattice. This mechanism would be very similar to the exsolution of hematite in plagioclase feldspar giving rise to the golden colour of sunstone. In the case of plagioclase, the hematite may become coarse enough to result in aventurescence. This phenomenon has not been observed in sapphire, although the process is not unlike the exsolution of titanium oxides (rutile) in corundum to produce the familiar silk inclusions. As noted above, however, detailed research will be needed to answer this question for certain.'

Here it was stated that the colour intensification of some golden yellow heat treated sapphires is in part thought to be the direct result of the presence of inclusions.

Another noteworthy paper discussing yellow and orange-brown heat-treated sapphires, authored by Dr Karl Schmetzer of West Germany, and George Bosshart and Dr Henry A. Hänni from Switzerland, was published in 1983.

In this paper the authors point out that although temperatures in excess of 1550°C are reportedly used in the annealing of yellow sapphires no explanation as to the cause of the heat treatment-generated yellow coloration can be given at this time. They then go on to speculate:

Possibly is it related to the resorption of pre-existent mineral inclusions during annealing. Chemical analyses (microprobe, X-ray fluorescence)

indicate limited contents of Fe and sometimes also of Cr and Mg. Already before the heat treatment, these elements were present in some form inside the crystal (as inclusion constituents or on Al sites of the corundum lattice) and become colour-efficient by the strong annealing.

Here again it is suggested that perhaps some inclusions in sapphires will supply their host with colouring ions during high temperature heat treatment.

In his definitive book *Gemstone enhancement* (1984) Dr Kurt Nassau also mentions inclusion caused colour in explaining that if pale to medium yellow corundum containing Fe^{3+} ions in the form of Fe_2O_3 is strongly heated it could aggregate the Fe_2O_3 to form particles of hematite and in this manner produce a deeper yellow-to-brown colour in the gem. One of the colour illustrations (by this author) in *Gemstone enhancement* (plate number XVI) shows orange-yellow halos in a heat-treated sapphire taken in diffused transmitted light at 25×.

What was not shown in the book was the matching companion micrograph taken in the same position, at the same magnification but under dark-field conditions. This second photomicrograph (Figure 1), when compared to the original photo shown in *Gemstone enhancement* (Figure 2), shows that for every orange-yellow halo there is a corresponding acicular inclusion at the centre of the halo. The connection here between inclusions, colour and heat treated host is obvious. The colouring agent (iron) has diffused from the inclusions into the surrounding sapphire.

Observations

After discovering this 'internal diffusion' colouring mechanism (Figure 3) twelve additional heat-treated yellow sapphires were examined very closely in both diffused transmitted and dark-field illumination using magnifications as high as 160×. In nine of the twelve treated sapphires tiny whitish appearing acicular inclusions, surrounded by yellow colour rinds, were observed. In the remaining three sapphires no specific source for the colour could be established.

Rutile (TiO_2 : often containing at least some iron), hematite ($\alpha-Fe_2O_3$: sometimes containing titanium) and ilmenite ($Fe^{+2}TiO_3$) have all been recognized as mineral inclusions in sapphires from various localities. Chemically they are also very closely related. Other chemically related inclusions such as pyrite (FeS_2), pyrrhotite ($Fe_{1-x}S$) and chalcopyrite ($CuFeS_2$) have also been identified in sapphires. Even though each of these compounds is universally acknowledged as a separate and distinct mineral, when studying their chemical formulas a common gemmological link is discovered. The

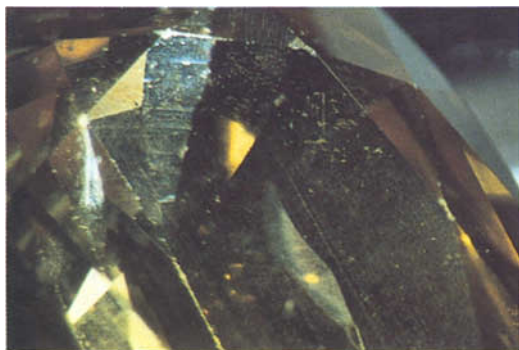


Fig. 1. Heat-treated orangish-yellow sapphire containing a multitude of tiny acicular (hematite?) inclusions. Dark-field illumination. 25x.



Fig. 2. Using diffused transmitted light on this same sapphire reveals an orangy-yellow coloured halo surrounding each of the minute whitish-appearing acicular inclusions. 25x.

metallic elements that compose them, either separately or together, have the capacity of causing yellow to blue colour in corundum. So perhaps if both iron and titanium (which are both necessary to create blue colour in sapphire) were present at the same time as the chemical components of an inclusion then a blue-coloured halo would be generated around that inclusion during high temperature heat treatment if the temperature was high enough to volatilize the inclusion without melting the host.

Just such an inclusion cannibalizing mechanism apparently does exist. An extensive microscopically-aided search through a number of pale to dark blue heat-treated sapphires from the Phillipsburg area of Montana in the United States (47 faceted stones) and from Sri Lanka (38 faceted stones) yielded a few gems (6 from Montana and 2 from Sri Lanka) that showed obvious evidence of blue internal-colour-diffusion haloing generated by thermally activated inclusions. Examples of this visual evidence of inclusion caused coloration in one of the heat-

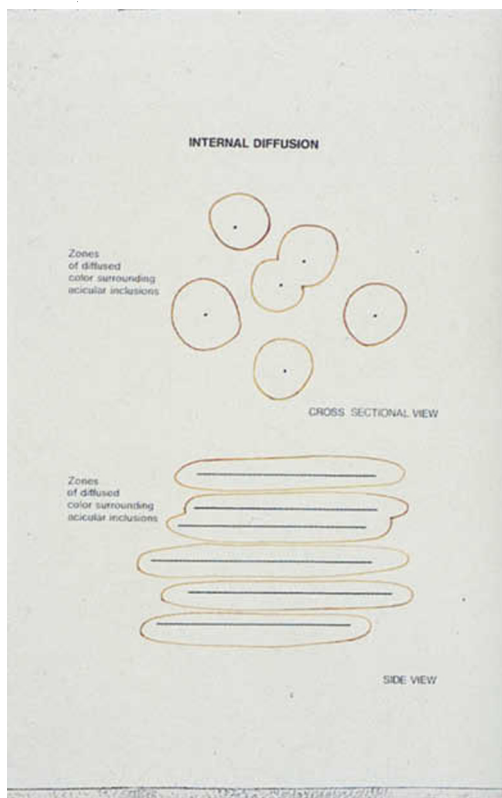


Fig. 3. Schematic diagram of the 'internal diffusion' mechanism showing both cross sectional and side views.

treated Phillipsburg sapphires is shown in Figure 4 while this same effect in a Sri Lankan gem is shown in Figure 5.

Additional examples of 'internal diffusion' have also been found while studying blue flame-fusion (Verneuil) synthetic sapphires. When the powdered chemicals which are melted to grow these synthetic sapphires are unevenly mixed small pockets of the chromophoric oxides used to produce the blue colour may become concentrated and trapped in the melt layers. When this happens, as shown in Figure 6, colour diffuses away from these pockets into the successive growth layers creating blue-phantoms extending from the oxide-pockets.

Conclusion

From the visual evidence presented in this study it is apparent that microscopically visible inclusions provide at least some of the colouring ions in some high temperature heat-treated sapphires through 'internal diffusion'. What percentage of the colour in a given gem can actually be attributed to this

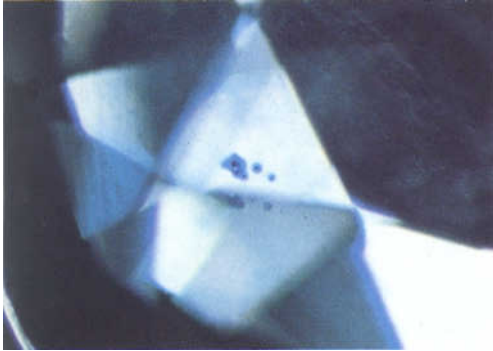


Fig. 4. (Above) Small cluster of anhedra black submetallic ilmenite inclusions encircled by blue 'internal diffusion' clouds in a pale blue sapphire from Phillipsburg, Montana. Diffused transmitted light. 45x.

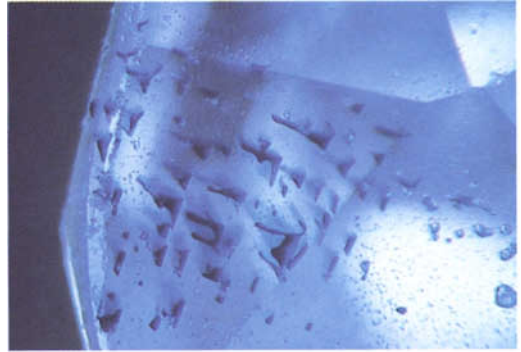


Fig. 5. (Above right) This tight grouping of irregular titaniferous hematite crystallites has released both titanium and iron during heat treatment resulting in the surrounding zone of blue colour in this Sri Lankan Sapphire. Diffused transmitted light. 40x.



Fig. 6. (Right) Chromophoric oxide-pockets with internal diffusion generated blue-phantoms in a flame-fusion synthetic sapphire. Diffused transmitted light. 35x.

mechanism is open to speculation and will differ from stone to stone. It is probable that most of the colour in heat-treated yellow and blue sapphires results from the presence of either trace elements or submicroscopic inclusions, neither of which can be observed with a microscope.

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